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Stress dependence of coercivity in nanocrystalline $Fe_{79}Hf_7B_{12}Si_2$ glass-coated microwires

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The stress dependence of the coercivity of thin $Fe_{79}Hf_7B_{12}Si_2$ glass-coated microwires exhibiting a nanocrystalline microstructure is presented. Such nanocrystalline microstructure was developed by means of 1 h annealing at temperatures between 450 and 600 °C. The evolution of the grain size (15–35 nm) with the annealing temperature was obtained from x-ray diffraction measurements. The applied tensile stress dependence of the coercive field of both as-cast and annealed samples has been measured. The coercivity monotonically decreases with the applied tensile stress for the as-cast and the low annealing temperature ($T_{ann} < 500$ °C) samples. This fact should be ascribed to the positive magnetostrictive character of these samples. Nevertheless, the samples annealed above 500 °C behave in the opposite sense, the coercivity increases with the applied tensile stress, as a consequence of the negative effective magnetostriction of the annealed samples with a massive presence of α-Fe(Si) and α-Fe nanograins. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2177131]

A nanocrystalline material can be considered as a polycrystalline solid formed by an isotropic distribution of nanometrically sized grains inside a residual amorphous matrix. Such structural description corresponds to the partial devitrification of the precursor amorphous material. In general, nanocrystals are connected between them by either grain boundaries or a different matrix. In the case of ferromagnetic nanocrystals, the matrix can be magnetic or not.

In accordance, Fe-based nanocrystalline alloys with very fine microstructure (with trademark Finemet), investigated by Yoshizawa *et al.*[1] can be considered as one of the best representative soft nanocrystalline materials. In fact, it combines high-saturation magnetization with very small coercive force and very low effective saturation magnetostriction.[2] These materials are characterized by a microstructure consisting basically of two phases, i.e., crystalline grains (with sizes of the order of tens of nanometers and random orientation of their easy axes) embedded in a residual amorphous matrix.[3] Such a microstructure is usually produced by partial

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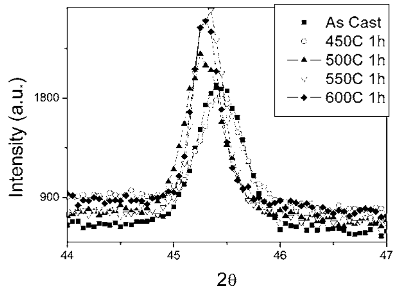

FIG. 1. Evolution of the main peak corresponding to (110) reflection of the XRD patterns of the $Fe_{79}Hf_7B_{12}Si_2$ glass-coated microwire with annealing.

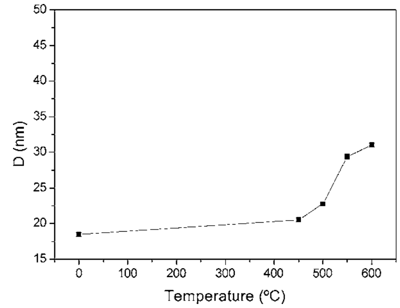

FIG. 2. Evolution of the average grain size of $Fe_{79}Hf_7B_{12}Si_2$ glass-coated microwire under annealing.

crystallization of the amorphous precursor. As it has been put in evidence by different studies, the basic mechanism leading to the achievement of such a good soft magnetic behavior is explained by the fact that the magnetocrystalline anisotropy of the randomly oriented nanocrystalline grains is averaged out by the exchange interactions.[4] Thus, the resulting magnetic behavior can be well described in the framework of the random anisotropy model.[5] According to this model, the very low values of the coercivity in the nanocrystalline state are ascribed to the small effective magnetic anisotropy (K_{eff} around 10 $\mathrm{J/m^3}$). Consequently, the excellent soft magnetic properties of these nanocrystalline biphase materials should be related to the strong coupling between the crystalline grains, which could be linked to a significant enhancement of the microstructure-magnetization interactions. These interactions, being originated in large units of coupled magnetic moments, suggest a relevant role of both the magnetostatic interactions as well as the formation of these coupled units.[6]

On the other hand, glass-covered microwires produced by means of a modified Taylor-Ulitovski method[7] have emerged as another family of magnetic materials very promising for technological applications.[8] Such magnetic microwire is a composite material containing, mainly, a metallic nucleus and a Pyrex-glass sheath. It is important to remark that the production method allows to produce tiny microwires with different geometries (that is, with different external diameter as well as different ratio between the diameter of the metallic nucleus and the external one) and different compositions of the metallic nucleus. Regarding the nature of the metallic nucleus, this method also presents the advantage of fabrication of glass-covered microwires with amorphous, nanocrystalline, and nanogranular characters.[8]

In this way, we have previously investigated Finemet glass-covered microwires[9,10] in order to compare the soft magnetic behavior with respect to conventional Finemet ribbons. As the most significant difference we have found that the insulating Pyrex-glass plays a very important role on the segregation of nanograins and, consequently, on the coercivity. In this paper we have investigated the microstructural and coercivity behavior of another composition, $Fe_{79}Hf_7B_{12}Si_2$, of glass-covered microwire.

Glass-covered microwires with the above mentioned composition were fabricated by the modified Taylor-Ulitovski method.[7] The total external diameter of the microwire was 24 μm and the one of the metallic nucleus was 15 μm. Pieces of 10 cm in length were annealed in the temperature range of 450–600 °C for 1 h.

The structural characteristics of the as-cast and annealed samples were obtained, at room temperature, from x-ray diffraction (XRD) technique by means of a powder diffractometer provided with an automatic divergence slit and a graphite monochromator with Cu $K\alpha$ radiation ($\lambda = 1.54$ Å). The measurements were carried out using the step scanning technique with steps of 0.05° (2θ) and accumulation times of 5 s. The hysteresis loops were obtained by means of a fluxmetric method described elsewhere.[10]

The evolution of the first peak of XRD with the annealing temperature is presented in the Fig. 1. As it can be seen, the position and width of such peaks change significantly with annealing. It is worth to mention that even the as-cast sample exhibits a slightly crystalline structure. The average grain size estimated from the peak width by means of Debye-Scherrer equation is about 17 nm.

The evolution of the average grain size of nanocrystals with the annealing temperature is presented in the Fig. 2. The grain size of the nanocrystals increases from about 17 up to 35 nm after annealing at 600 °C.

Figure 3 shows the hysteresis loop of the as-cast sample. As it can be observed, it presents rather elevated coercivity H_{c0}. Figure 4 shows the changes of the coercive field H_{c0} with the annealing temperature. In the range of 500–600 °C a significant enhancement of the soft magnetic character takes place, which results to coincide with the increase of the grain size D (see Fig. 1). Nevertheless, the values of $H_{c0} \approx 600$ A/m and $D \approx 30$ nm for these annealed samples (500–600 °C) are quite larger than those reported in the classical Finemet Fe-rich nanocrystalline ribbon shaped material ($H_c \approx 1$ A/m and $D \approx 10$ nm).[1] These differences could be associated to the strength and complexity of the internal stresses actuating on the metallic nucleus due to the glass coating. Such internal stresses give rise to some ordering to hinder the nanocrystallization process as it has been previ-

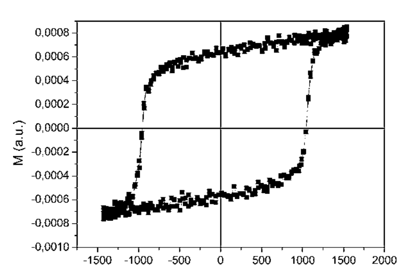

FIG. 3. Hysteresis loop of $Fe_{79}Hf_7B_{12}Si_2$ glass-coated microwire in the as-prepared state.

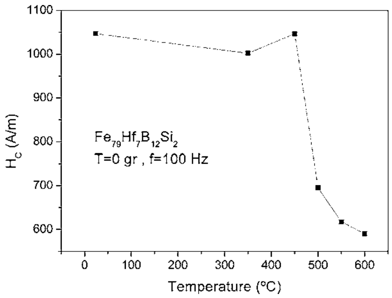

FIG. 4. Evolution of the coercivity of $Fe_{79}Hf_7B_{12}Si_2$ glass-coated microwire under annealing.

ously observed in glass-coated Finemet-type microwires.[10]

The stress dependences of the coercivity for all, as-cast and annealed, samples are shown in the Fig. 5. The dependence of $(H_{c0}-H_{cS})/H_{cS}$ (H_{c0} is the coercivity without stress and H_{cS} is the coercivity under stress) with the applied stress σ_a is shown. The applied stresses acting on the metallic nucleus have been calculated in accordance to Ref. 11. H_c decreases with σ_a in the as-cast and annealed samples at low annealing temperatures (<500 °C), while in samples treated above 500 °C, H_c increases with σ_a. This behavior should be linked to the different magnetostrictive characters of the samples. In fact, the effective saturation magnetostriction in soft nanocrystalline alloys has been assumed to be a balance of two main opposite contributions, namely, the first one arising from the partial volume of nanocrystalline phases and the second one arising from the residual amorphous matrix.[12] Therefore, it can logically be assumed that the content and the distribution of the nanocrystalline and amorphous phases change with the annealing, giving rise to different stress dependences of the coercivity. In the as-cast and low temperature annealed samples ($T_{ann}<500$ °C) the coercivity monotonically decreases with the applied tensile stress, which should be connected to the positive magnetostrictive character of these samples, while in the samples annealed above 500 °C the coercivity behaves in an opposite way, being increased with σ_a, as a consequence of the negative effective magnetostriction in the annealed samples, characterized by the massive presence of nanograins.

In addition, the increase of the grain size (15–35 nm) with the simultaneous decrease of the coercivity seems to indicate some kind of deviation from the random anisotropy model proposed by Herzer for the nanocrystalline Finemet material.[12] According to such model, an enhanced magnetic

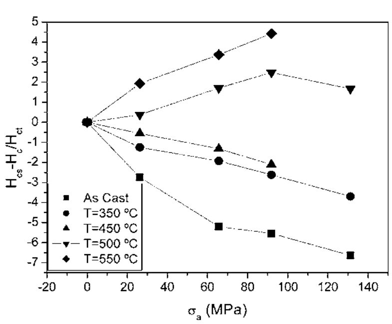

FIG. 5. Stress dependence of the coercivity of $Fe_{79}Hf_7B_{12}Si_2$ glass-coated microwire in the as-prepared state and after annealing at different temperatures.

softness correlates with the grain size and the best magnetic softness achieved under conditions of averaging grain size, typically of 10–15 nm, is much below than the exchange correlation length, being around 35–40 nm. These differences could be ascribed to the strength and complexity of the internal stresses acting on the metallic nucleus due to the glass coating. Another reason to explain the relationship between the grain size and the coercivity obtained for these thermally treated microwires could be assigned to the difference of the volume fraction of the α-Fe phase. In fact, the devitrification starts above 450 °C (see Figs. 1 and 5). Therefore, the crystalline volume fraction and the size of the crystallites increase above 450 °C. Consequently, the exchange coupling occurs almost directly between crystals and the random anisotropy model efficiently works to decrease the coercivity. However, in the annealed samples below 450 °C, the crystalline phase is embedded in the amorphous phase and the coupling occurs through the last one; therefore, the observed behavior of H_c is mainly due to the amorphous phase.

We can conclude that the nanocrystalline $Fe_{79}Hf_7B_{12}Si_2$ thin glass-coated microwire has been successfully fabricated. An improvement of the magnetic softness of nanocrystalline $Fe_{79}Hf_7B_{12}Si_2$ glass-coated microwire under annealing has been observed and analyzed. The comparison of XRD results with the magnetic properties shows that the nanocrystalline samples cannot develop the extremely soft magnetic behavior as nanocrystalline Fe-rich ribbons and thin wires do. Such differences can be attributed to the internal stresses arising from the glass-covered sheath as well as to the small diameter of the studied samples. Nevertheless, the control of the nanostructure from careful thermal treatments leads to significant improvement of the coercivity. The results concerning the stress dependence of the coercive field of the as-cast and annealed samples are interpreted in terms of different magnetostrictive characters induced by annealing at temperatures lower or higher than 500 °C which are straightforwardly related to the massive presence of α-Fe(Si) and α-Fe nanograins.

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